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<p>(54) Title: FUEL ADDITIVE COMPOSITIONS CONTAINING POLY(OXYALKYLENE) AMINES AND POLYALKYL HYDROXYAROMATICS</p> <p>(57) Abstract</p> <p>A fuel additive composition comprising: a) a poly(oxyalkylene) amine having at least one basic nitrogen and a sufficient number of oxyalkylene units to render the poly(oxyalkylene) amine soluble in hydrocarbons boiling in the gasoline or diesel range; and b) a polyalkyl hydroxyaromatic compound or salt thereof wherein the polyalkyl group has sufficient molecular weight and carbon chain length to render the polyalkyl hydroxyaromatic compound soluble in hydrocarbons boiling in the gasoline or diesel range.</p>		

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01 FUEL ADDITIVE COMPOSITIONS CONTAINING
02 POLY(OXYALKYLENE) AMINES
03 AND POLYALKYL HYDROXYAROMATICS
04

05 BACKGROUND OF THE INVENTION
06

07 This invention relates to a fuel additive composition. More
08 particularly, this invention relates to a fuel additive
09 composition containing a poly(oxyalkylene) amine and a
10 polyalkyl hydroxyaromatic compound.
11

12 It is well known in the art that liquid hydrocarbon
13 combustion fuels, such as fuel oils and gasolines, tend to
14 exhibit certain deleterious characteristics, either after
15 long periods of storage or under actual operational
16 conditions. Gasolines, for example, in operational use tend
17 to deposit sludge and varnish at various points in the power
18 system, including the carburetor or injectors and the intake
19 valves. It is desirable, therefore, to find a means for
20 improving liquid hydrocarbon fuels by lessening their
21 tendency to leave such deposits.
22

23 U.S. Patent No. 3,849,085 discloses a motor fuel composition
24 comprising a mixture of hydrocarbon in the gasoline boiling
25 range containing about 0.01 to 0.25 volume percent of a high
26 molecular weight aliphatic hydrocarbon substituted phenol in
27 which the aliphatic hydrocarbon radical has an average
28 molecular weight in the range of about 500 to 3,500. This
29 patent teaches that gasoline compositions containing a minor
30 amount of an aliphatic hydrocarbon substituted phenol not
31 only prevents or inhibits the formation of intake valve and
32 port deposits in a gasoline engine but also enhances the
33 performance of the fuel composition in engines designed to
34 operate at higher operating temperatures with a minimum of

01 decomposition and deposit formation in the manifold of the
02 engine.
03
04 U.S. Patent No. 4,134,846 discloses a fuel additive
05 composition comprising a mixture of (1) the reaction product
06 of an aliphatic hydrocarbon-substituted phenol,
07 epichlorohydrin and a primary or secondary mono- or
08 polyamine, and (2) a polyalkylene phenol. This patent
09 teaches that such compositions show excellent carburetor,
10 induction system and combustion chamber detergency and, in
11 addition, provide effective rust inhibition when used in
12 hydrocarbon fuels at low concentrations.

13

14 SUMMARY OF THE INVENTION

15

16 The present invention provides a novel fuel additive
17 composition comprising:

18

19 (a) a poly(oxyalkylene) amine having at least one basic
20 nitrogen atom and a sufficient number of oxyalkylene
21 units to render the poly(oxyalkylene) amine soluble in
22 hydrocarbons boiling in the gasoline or diesel range,
23 and

24

25 (b) a polyalkyl hydroxyaromatic compound or salt thereof
26 wherein the polyalkyl group has sufficient molecular
27 weight and carbon chain length to render the polyalkyl
28 hydroxyaromatic compound soluble in hydrocarbons
29 boiling in the gasoline or diesel range.

30

31 The present invention further provides a fuel composition
32 comprising a major amount of hydrocarbons boiling in the
33 gasoline or diesel range and an effective detergent amount
34 of the novel fuel additive composition described above.

01 The present invention is also concerned with a fuel
02 concentrate comprising an inert stable oleophilic organic
03 solvent boiling in the range of from about 150°F to 400°F
04 and from about 10 to 70 weight percent of the fuel additive
05 composition of the instant invention.

06

07 Among other factors, the present invention is based on the
08 surprising discovery that the unique combination of a
09 poly(oxyalkylene) amine and a polyalkyl hydroxyaromatic
10 compound provides unexpectedly superior deposit control
11 performance when compared to each component individually.

12

13

DETAILED DESCRIPTION OF THE INVENTION

14

15

The Poly(oxyalkylene) Amine

16

17 As noted above, the poly(oxyalkylene) amine component of the
18 present fuel additive composition is a poly(oxyalkylene)
19 amine having at least one basic nitrogen atom and a
20 sufficient number of oxyalkylene units to render the
21 poly(oxyalkylene) amine soluble in hydrocarbons boiling in
22 the gasoline or diesel range. Preferably, such
23 poly(oxyalkylene) amines will also be of sufficient
24 molecular weight so as to be nonvolatile at normal engine
25 intake valve operating temperatures, which are generally in
26 the range of about 175°C to 300°C.

27

28 Generally, the poly(oxyalkylene) amines suitable for use in
29 the present invention will contain at least about 5
30 oxyalkylene units, preferably about 5 to 100, more
31 preferably about 8 to 100, and even more preferably about 10
32 to 100. Especially preferred poly(oxyalkylene) amines will
33 contain about 10 to 25 oxyalkylene units.

34

01 The molecular weight of the presently employed
02 poly(oxyalkylene) amines will generally range from about 500
03 to about 10,000, preferably from about 500 to about 5,000.
04
05 Suitable poly(oxyalkylene) amine compounds include
06 hydrocarbyl poly(oxyalkylene) polyamines as disclosed, for
07 example, in U.S. Patent No. 4,247,301 to Honnen, the
08 disclosure of which is incorporated herein by reference.
09 These compounds are hydrocarbyl poly(oxyalkylene) polyamines
10 wherein the poly(oxyalkylene) moiety comprises at least one
11 hydrocarbyl-terminated poly(oxyalkylene) chain of 2 to 5
12 carbon atom oxyalkylene units, and wherein the
13 poly(oxyalkylene) chain is bonded through a terminal carbon
14 atom to a nitrogen atom of a polyamine having from 2 to
15 about 12 amine nitrogen atoms and from 2 to about 40 carbon
16 atoms with a carbon-to-nitrogen ratio between about 1:1 and
17 10:1. The hydrocarbyl group on these hydrocarbyl
18 poly(oxyalkylene) polyamines will contain from about 1 to 30
19 carbon atoms. These compounds generally have molecular
20 weights in the range of about 500 to 10,000, preferably from
21 about 500 to 5,000 and more preferably from about 800 to
22 5,000.
23
24 The above-described hydrocarbyl poly(oxyalkylene) polyamines
25 are prepared by conventional procedures known in the art, as
26 taught, for example, in U.S. Patent No. 4,247,301.
27
28 Other poly(oxyalkylene) amines suitable for use in the
29 present invention are the poly(oxyalkylene) polyamines
30 wherein the poly(oxyalkylene) moiety is connected to the
31 polyamine moiety through an oxyalkylene hydroxy-type linkage
32 derived from an epihalohydrin, such as epichlorohydrin or
33 epibromohydrin. This type of poly(oxyalkylene) amine having
34 an epihalohydrin-derived linkage is described, for example,

01 in U.S. Patent No. 4,261,704, the disclosure of which is
02 incorporated herein by reference.

03
04 Useful polyamines for preparing the epihalohydrin-derived
05 poly(oxyalkylene) polyamines include, for example, alkylene
06 polyamines, polyalkylene polyamines, cyclic amines, such as
07 piperazines, and amino-substituted amines. The
08 poly(oxyalkylene) polyamines having an epihalohydrin-derived
09 linkage between the poly(oxyalkylene) and polyamine moieties
10 are prepared using known procedures as taught, for example,
11 in U.S. Patent No. 4,261,704.

12
13 Another type of poly(oxyalkylene) amine useful in the
14 present invention is a highly branched alkyl
15 poly(oxyalkylene) monoamine as described, for example in
16 published European Patent Application No. 0,448,365 A1,
17 published September 25, 1991, the disclosure of which is
18 incorporated herein by reference. These highly branched
19 alkyl poly(oxyalkylene) monoamines have the general formula:



22
23 wherein R is a highly branched alkyl group containing from
24 12 to 40 carbon atoms, preferably an alkyl group having 20
25 carbon atoms which is derived from a Guerbet condensation
26 reaction, and x is a number up to 30, preferably 4 to 8.
27 The preferred alkyl group is derived from a Guerbet alcohol
28 containing 20 carbon atoms having the formula:



31
32
33 wherein R'' is a hydrocarbyl chain.

34

01 The above highly branched alkyl poly(oxyalkylene) monoamines
02 are prepared by using known methods as disclosed, for
03 example, in European Patent Application No. 0,448,365 A1.

04

05 A preferred class of poly(oxyalkylene) amine suitable for
06 use in the composition of the present invention is the
07 hydrocarbyl-substituted poly(oxyalkylene) aminocarbamate
08 disclosed, for example, in U.S. Patent Nos. 4,288,612;
09 4,236,020; 4,160,648; 4,191,537; 4,270,930; 4,233,168;
10 4,197,409; 4,243,798 and 4,881,945, the disclosure of each
11 of which are incorporated herein by reference. These
12 hydrocarbyl poly(oxyalkylene) aminocarbamates will contain
13 at least one basic nitrogen atom and have an average
14 molecular weight of about 500 to 10,000, preferably about
15 500 to 5,000, and more preferably about 1,000 to 3,000. As
16 discussed more fully below, these hydrocarbyl
17 poly(oxyalkylene) aminocarbamates can be said to contain a
18 poly(oxyalkylene) component, an amine component and a
19 carbamate connecting group.

20

21 A. The Poly(oxyalkylene) Component

22

23 The hydrocarbyl-terminated poly(oxyalkylene) polymers which
24 are utilized in preparing the amino carbamates employed in
25 the present invention are monohydroxy compounds, e.g.,
26 alcohols, often termed monohydroxy polyethers, or
27 polyalkylene glycol monocarbyl ethers, or "capped"
28 poly(oxyalkylene) glycols, and are to be distinguished from
29 the poly(oxyalkylene) glycols (diols), or polyols, which are
30 not hydrocarbyl-terminated, i.e., are not capped. The
31 hydrocarbyl-terminated poly(oxyalkylene) alcohols are
32 produced by the addition of lower alkylene oxides, such as
33 oxirane, ethylene oxide, propylene oxide, butylene oxide,
34 etc. to the hydroxy compound, ROH, under polymerization

01 conditions, wherein R is the hydrocarbyl group which caps
02 the poly(oxyalkylene) chain. In the poly(oxyalkylene)
03 component employed in the present invention, the group R
04 will generally contain from 1 to about 30 carbon atoms,
05 preferably from 2 to about 20 carbon atoms and is preferably
06 aliphatic or aromatic, i.e., an alkyl or alkyl phenyl
07 wherein the alkyl is a straight or branched-chain of from
08 1 to about 24 carbon atoms. More preferably, R is
09 alkylphenyl wherein the alkyl group is a branched-chain of
10 12 carbon atoms, derived from propylene tetramer, and
11 commonly referred to as tetrapropenyl. The oxyalkylene
12 units in the poly(oxyalkylene) components preferably contain
13 from 2 to about 5 carbon atoms but one or more units of a
14 larger carbon number may also be present. Generally, each
15 poly(oxyalkylene) polymer contains at least about 5
16 oxyalkylene units, preferably about 5 to about 100
17 oxyalkylene units, more preferably about 8 to about 100
18 units, even more preferably about 10 to 100 units, and most
19 preferably 10 to about 25 such units. The poly(oxyalkylene)
20 component employed in the present invention is more fully
21 described and exemplified in U.S. Patent No. 4,191,537, the
22 disclosure of which is incorporated herein by reference.

23
24 Although the hydrocarbyl group on the hydrocarbyl
25 poly(oxyalkylene) component will preferably contain from
26 1 to about 30 carbon atoms, longer hydrocarbyl groups,
27 particularly longer chain alkyl phenyl groups, may also be
28 employed.

29
30 For example, alkylphenyl poly(oxyalkylene) aminocarbamates
31 wherein the alkyl group contains at least 40 carbon atoms,
32 as described in U.S. Patent No. 4,881,945 to Buckley, are
33 also contemplated for use in the present invention. The
34 alkyl phenyl group on the aminocarbamates of U.S. Patent

01 No. 4,881,945 will preferably contain an alkyl group of
02 50 to 200 carbon atoms, and more preferably, an alkyl group
03 of 60 to 100 carbon atoms. The disclosure of U.S. Patent
04 No. 4,881,945 is incorporated herein by reference.

05
06 Also, contemplated for use in the present invention are
07 alkylphenyl poly(oxypropylene) aminocarbamates wherein the
08 alkyl group is a substantially straight-chain alkyl group
09 of about 25 to 50 carbon atoms derived from an alpha olefin
10 oligomer of C₄ to C₂₀ alpha olefins, as described in
11 PCT International Patent Application Publication No. WO
12 90/07564, published July 12, 1990, the disclosure of which
13 is incorporated herein by reference.

14
15 B. The Amine Component

16
17 The amine moiety of the hydrocarbyl-terminated
18 poly(oxyalkylene) aminocarbamate is preferably derived from
19 a polyamine having from 2 to about 12 amine nitrogen atoms
20 and from 2 to about 40 carbon atoms. The polyamine is
21 preferably reacted with a hydrocarbyl poly(oxyalkylene)
22 chloroformate to produce the hydrocarbyl poly(oxyalkylene)
23 aminocarbamate fuel additive finding use within the scope of
24 the present invention. The chloroformate is itself derived
25 from hydrocarbyl poly(oxyalkylene) alcohol by reaction with
26 phosgene. The polyamine, encompassing diamines, provides
27 the product poly(oxyalkylene) aminocarbamate with, on the
28 average, at least about one basic nitrogen atom per
29 carbamate molecule, i.e., a nitrogen atom titratable by
30 strong acid. The polyamine preferably has a carbon-to-
31 nitrogen ratio of from about 1:1 to about 10:1. The
32 polyamine may be substituted with substituents selected from
33 hydrogen, hydrocarbyl groups of from 1 to about 10 carbon
34 atoms, acyl groups of from 2 to about 10 carbon atoms, and

01 monoketone, monohydroxy, mononitro, monocyano, alkyl and
02 alkoxy derivatives of hydrocarbyl groups of from 1 to 10
03 carbon atoms. It is preferred that at least one of the
04 basic nitrogen atoms of the polyamine is a primary or
05 secondary amino nitrogen. The polyamine component employed
06 in the present invention has been described and exemplified
07 more fully in U.S. Patent No. 4,191,537.

08

09 Hydrocarbyl, as used in describing the hydrocarbyl
10 poly(oxyalkylene) and amine components used in this
11 invention, denotes an organic radical composed of carbon and
12 hydrogen which may be aliphatic, alicyclic, aromatic or
13 combinations thereof, e.g., aralkyl. Preferably, the
14 hydrocarbyl group will be relatively free of aliphatic
15 unsaturation, i.e., ethylenic and acetylenic, particularly
16 acetylenic unsaturation. The more preferred polyamine
17 finding use within the scope of the present invention is a
18 polyalkylene polyamine, including alkylenediamine, and
19 including substituted polyamines, e.g., alkyl and
20 hydroxyalkyl-substituted polyalkylene polyamine.

21 Preferably, the alkylene group contains from 2 to 6 carbon
22 atoms, there being preferably from 2 to 3 carbon atoms
23 between the nitrogen atoms. Examples of such polyamines
24 include ethylenediamine, diethylene triamine, triethylene
25 tetramine, di(trimethylene) triamine, dipropylene triamine,
26 tetraethylene pentamine, etc. Among the polyalkylene
27 polyamines, polyethylene polyamine and polypropylene
28 polyamine containing 2-12 amine nitrogen atoms and 2-24
29 carbon atoms are especially preferred and in particular, the
30 lower polyalkylene polyamines, e.g., ethylenediamine,
31 diethylene triamine, propylene diamine, dipropylene
32 triamine, etc., are most preferred.

33

34

01 C. The Aminocarbamate

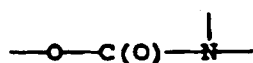
02

03 The poly(oxyalkylene) aminocarbamate fuel additive used in
04 compositions of the present invention is obtained by linking
05 the amine component and the poly(oxyalkylene) component
06 together through a carbamate linkage, i.e.,

07

08

09



10

11 wherein the oxygen may be regarded as the terminal hydroxyl
12 oxygen of the poly(oxyalkylene) alcohol component, and the
13 carbonyl group ---C(O)--- , is preferably provided by a
14 coupling agent, e.g., phosgene. In the preferred method of
15 preparation, the hydrocarbyl poly(oxyalkylene) alcohol is
16 reacted with phosgene to produce a chloroformate and the
17 chloroformate is reacted with the polyamine. The carbamate
18 linkages are formed as the poly(oxyalkylene) chains are
19 bound to the nitrogen of the polyamine through the
20 oxycarbonyl group of the chloroformate. Since there may be
21 more than one nitrogen atom of the polyamine which is
22 capable of reacting with the chloroformate, the
23 aminocarbamate contains at least one hydrocarbyl
24 poly(oxyalkylene) polymer chain bonded through an
25 oxycarbonyl group to a nitrogen atom of the polyamine, but
26 the carbonate may contain from 1 to 2 or more such chains.
27 It is preferred that the hydrocarbyl poly(oxyalkylene)
28 aminocarbamate product contains on the average, about
29 1 poly(oxyalkylene) chain per molecule (i.e., is a
30 monocarbamate), although it is understood that this reaction
31 route may lead to mixtures containing appreciable amounts of
32 di or higher poly(oxyalkylene) chain substitution on a
33 polyamine containing several reactive nitrogen atoms. A
34 particularly preferred aminocarbamate is alkylphenyl

01 poly(oxybutylene) aminocarbamate, wherein the amine moiety
02 is derived from ethylene diamine or diethylene triamine.
03 Synthetic methods to avoid higher degrees of substitution,
04 methods of preparation, and other characteristics of the
05 aminocarbamates used in the present invention are more fully
06 described and exemplified in U.S. Patent No. 4,191,537.

07

08

The Polyalkyl Hydroxyaromatic Compound

09

10 As noted above, the polyalkyl hydroxyaromatic component of
11 the present fuel additive composition is a polyalkyl
12 hydroxyaromatic compound or salt thereof wherein the
13 polyalkyl group has sufficient molecular weight and carbon
14 chain length to render the polyalkyl hydroxyaromatic
15 compound soluble in hydrocarbons boiling in the gasoline or
16 diesel range. As with the poly(oxyalkylene) amine component
17 of the present invention, the polyalkyl hydroxyaromatic
18 compound will preferably be of sufficient molecular weight
19 so as to be nonvolatile at normal engine intake valve
20 operating temperatures, generally in the range of about
21 175°C to 300°C.

22

23 In general, the polyalkyl substituent on the polyalkyl
24 hydroxyaromatic compound will have an average molecular
25 weight in the range of about 400 to 5,000, preferably about
26 400 to 3,000, more preferably from about 600 to 2,000.

27

28 The polyalkyl-substituted hydroxyaromatic compounds finding
29 use in this invention are derived from hydroxyaromatic
30 hydrocarbons. Such hydroxyaromatic compounds include
31 mononuclear monohydroxy and polyhydroxy aromatic
32 hydrocarbons having 1 to 4, and preferably 1 to 3, hydroxy
33 groups. Suitable hydroxyaromatic compounds include phenol,

34

01 catechol, resorcinol, hydroquinone, pyrogallol, and the
02 like. The preferred hydroxyaromatic compound is phenol.

03

04 Suitable polyalkyl hydroxyaromatic compounds and their
05 preparation are described, for example, in U.S. Patent
06 Nos. 3,849,085; 4,231,759 and 4,238,628, the disclosures of
07 each of which are incorporated herein by reference.

08

09 The polyalkyl substituent on the polyalkyl hydroxyaromatic
10 compounds employed in the invention may be generally derived
11 from polyolefins which are polymers or copolymers of
12 mono-olefins, particularly 1-mono-olefins, such as ethylene,
13 propylene, butylene, and the like. Preferably, the
14 mono-olefin employed will have 2 to about 24 carbon atoms,
15 and more preferably, about 3 to 12 carbon atoms. More
16 preferred mono-olefins include propylene, butylene,
17 particularly isobutylene, 1-octene and 1-decene.
18 Polyolefins prepared from such mono-olefins include
19 polypropylene, polybutene, especially polyisobutene, and the
20 polyalphaolefins produced from 1-octene and 1-decene.

21

22 The preferred polyisobutenes used to prepare the presently
23 employed polyalkyl hydroxyaromatic compounds are
24 polyisobutenes which comprise at least about 20% of the more
25 reactive methylvinylidene isomer, preferably at least 50%
26 and more preferably at least 70%. Suitable polyisobutenes
27 include those prepared using BF₃ catalysts. The preparation
28 of such polyisobutenes in which the methylvinylidene isomer
29 comprises a high percentage of the total composition is
30 described in U.S. Patent Nos. 4,152,499 and 4,605,808.

31

32 Examples of suitable polyisobutenes having a high
33 alkylvinylidene content include Ultravis 30, a polyisobutene
34 having a molecular weight of about 1300 and a

01 methylvinylidene content of about 74%, available from
02 British Petroleum.

03

04 Numerous methods are known for preparing the polyalkyl
05 hydroxyaromatic compounds used in the present invention and
06 any of these are considered suitable for producing the
07 polyalkyl hydroxyaromatic component of the instant fuel
08 additive composition. One such method involves the reaction
09 of a phenol with an olefin polymer in the presence of an
10 aluminum chloride-sulfuric acid catalyst, as described in
11 U.S. Patent No. 3,849,085. Similarly, U.S. Patent
12 No. 4,231,759 discloses that polyalkyl hydroxyaromatic
13 compounds may be obtained by the alkylation of phenol with
14 polypropylene, polybutylene and other polyalkylene
15 compounds, in the presence of an alkylation catalyst, such
16 as boron trifluoride.

17

18 One preferred method of preparing polyalkyl hydroxyaromatic
19 compounds is disclosed in U.S. Patent No. 4,238,628. This
20 patent teaches a process for producing undegraded alkylated
21 phenols by alkylating, at about 0°C to 60°C, a complex
22 comprising boron trifluoride and phenol with a propylene or
23 higher olefin polymer having terminal ethylene units,
24 wherein the molar ratio of complex to olefin polymer is
25 about 1:1 to 3:1. Preferred olefin polymers include
26 polybutene having terminal ethylene units.

27

28 Preferred polyalkyl hydroxyaromatic compounds finding use in
29 the fuel additive composition of the present invention
30 include polypropylene phenol, polyisobutylene phenol, and
31 polyalkyl phenols derived from polyalphaolefins,
32 particularly 1-decene oligomers.

33

34

-14-

01 Polyalkyl phenols, wherein the polyalkyl group is derived
02 from polyalphaolefins, such as 1-octene and 1-decene
03 oligomers, are described in PCT International Patent
04 Application Publication No. WO 90/07564, published July 12,
05 1990, the disclosure of which is incorporated herein by
06 reference. This publication teaches that such polyalkyl
07 phenols may be prepared by reacting the appropriate
08 polyalphaolefin with phenol in the presence of an alkylating
09 catalyst at a temperature of from about 60°C to 200°C,
10 either neat or in an inert solvent at atmospheric pressure.
11 A preferred alkylation catalyst for this reaction is a
12 sulfonic acid catalyst, such as Amberlyst 15®, available
13 from Rohm and Haas, Philadelphia, Pennsylvania.

14
15 Also contemplated for use in the present fuel additive
16 composition are the salts of the polyalkyl hydroxyaromatic
17 component, such as alkali metal, alkaline earth metal,
18 ammonium, substituted ammonium and sulfonium salts.
19 Preferred salts are the alkali metal salts of the polyalkyl
20 hydroxyaromatic compound, particularly the sodium and
21 potassium salts, and the substituted ammonium salts.

22 Fuel Compositions

23
24
25 The fuel additive composition of the present invention will
26 generally be employed in a hydrocarbon distillate fuel
27 boiling in the gasoline or diesel range. The proper
28 concentration of this additive composition necessary in
29 order to achieve the desired detergency and dispersancy
30 varies depending upon the type of fuel employed, the
31 presence of other detergents, dispersants and other
32 additives, etc. Generally, however, from 150 to 7500 weight
33 ppm, preferably from 300 to 2500 ppm, of the present
34

01 additive composition per part of base fuel is needed to
02 achieve the best results.

03

04 In terms of individual components, fuel compositions
05 containing the additive compositions of the invention will
06 generally contain about 50 to 2500 ppm of the
07 poly(oxyalkylene) amine and about 100 to 5000 ppm of the
08 polyalkyl hydroxyaromatic compound. The ratio of polyalkyl
09 hydroxyaromatic to poly(oxyalkylene) amine will generally
10 range from about 0.5 to 10:1, and will preferably be about
11 2:1 or greater.

12

13 The deposit control additive may be formulated as a
14 concentrate, using an inert stable oleophilic organic
15 solvent boiling in the range of about 150°F to 400°F.
16 Preferably, an aliphatic or an aromatic hydrocarbon solvent
17 is used, such as benzene, toluene, xylene or higher-boiling
18 aromatics or aromatic thinners. Aliphatic alcohols of about
19 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol,
20 n-butanol and the like, in combination with hydrocarbon
21 solvents are also suitable for use with the detergent-
22 dispersant additive. In the concentrate, the amount of the
23 present additive composition will be ordinarily at least 10%
24 by weight and generally not exceed 70% by weight, preferably
25 10 to 50 weight percent and most preferably from 10 to 25
26 weight percent.

27

28 In gasoline fuels, other fuel additives may also be included
29 such as antiknock agents, e.g., methylcyclopentadienyl
30 manganese tricarbonyl, tetramethyl or tetraethyl lead, or
31 other dispersants or detergents such as various substituted
32 amines, etc. Also included may be lead scavengers such as
33 aryl halides, e.g., dichlorobenzene or alkyl halides, e.g.,
34 ethylene dibromide. Additionally, antioxidants, metal

01 deactivators, pour point depressants, corrosion inhibitors
02 and demulsifiers may be present.

03

04 In diesel fuels, other well-known additives can be employed,
05 such as pour point depressants, flow improvers, cetane
06 improvers, and the like.

07

08 The following examples are presented to illustrate specific
09 embodiments of this invention and are not to be construed in
10 any way as limiting the scope of the invention.

11

12

EXAMPLES

13

14

Example 1

15

16

Preparation of Polyisobutyl Phenol

17

18 To a flask equipped with a magnetic stirrer, reflux
19 condenser, thermometer, addition funnel and nitrogen inlet
20 was added 203.2 grams of phenol. The phenol was warmed to
21 40°C and the heat source was removed. Then,
22 73.5 milliliters of boron trifluoride etherate was added
23 dropwise. Ultravis 10 polyisobutene (molecular weight 950,
24 76% methylvinylidene, available from British Petroleum) was
25 dissolved in 1,863 milliliters of hexane. The polyisobutene
26 was added to the reaction at a rate to maintain the
27 temperature between 22-27°C. The reaction mixture was
28 stirred for 16 hours at room temperature. Then,
29 400 milliliters of concentrated ammonium hydroxide was added
30 followed by 2,000 milliliters of hexane. The reaction
31 mixture was washed with water (3 x 2,000 milliliters), dried
32 over magnesium sulfate, filtered and the solvents removed
33 under vacuum to yield 1,056.5 grams of a crude reaction
34 product. The crude reaction product was determined to

-17-

01 contain 80% of the desired product by proton NMR and
02 chromatography on silica gel eluting with hexane, followed
03 by hexane: ethylacetate: ethanol (93:5:2).
04

05 Example 2

06
07 Thermogravimetric Analysis
08

09 The stability of certain fuel additives was measured by
10 thermogravimetric analysis (TGA). The TGA procedure
11 employed DuPont 951 TGA instrumentation coupled with a
12 microcomputer for data analysis. Samples of the fuel
13 additive (approximately 25 milligrams) were heated from 25°C
14 to 700°C at 5°C per minute under air flowing at 100 cubic
15 centimeters per minute. The weight of the sample was
16 monitored as a function of temperature. The thermal
17 stability of various samples was compared at fifty percent
18 weight loss. Sample 1 was a tetrapropenylphenyl
19 poly(oxybutylene) ethylene diamine carbamate having a
20 molecular weight of about 1718, prepared in a manner similar
21 to that described in U.S. Patent No. 4,160,648 to Lewis,
22 Examples 6-8. Sample 2 was a polyisobutyl phenol prepared
23 from Ultravis 30 polyisobutene (molecular weight 1300, 74%
24 methylvinylidene, available from British Petroleum) in a
25 manner similar to Example 1 above.
26

27 The fifty percent weight loss temperature for Sample 1,
28 tetrapropenylphenyl poly(oxybutylene) ethylenediamine
29 carbamate, was 259°C. The fifty percent weight loss
30 temperature for Sample 2, polyisobutyl phenol, was 347°C. A
31 one-to-one mixture of the two components, Samples 1 and 2,
32 was analyzed by TGA. The twenty-five percent weight loss
33 temperature (50% weight loss of tetrapropenylphenyl
34 poly(oxybutylene) ethylenediamine carbamate in the mixture)

01 was 296°C. This demonstrates that the thermal stability of
02 the tetrapropenylphenyl poly(oxybutylene) ethylenediamine
03 carbamate is increased by the presence of the polyisobutyl
04 phenol. This increase in thermal stability allows the
05 tetrapropenylphenyl poly(oxybutylene) ethylenediamine
06 carbamate to last longer at intake valve operating
07 temperatures and allows for less deposits.

08

09

Example 3

10

11

Engine Test

12

13 A laboratory engine test was used to evaluate both intake
14 valve and combustion chamber deposit performance of the
15 additive composition of the invention. The test engine is a
16 4.3 liter, TBI (throttle body injected), V6 engine
17 manufactured by General Motors Corporation.

18

19 The major engine dimensions are listed below:

20

21

22

23

24

25

26

27

28

29 The test procedure involves engine operation for 40 hours
30 (24 hours a day) on a prescribed load and speed schedule
31 representative of typical driving conditions. The cycle for
32 engine operation during the test is as follows:

33

34

Table I - Engine Dimensions	
Bore	10.16 cm
Stroke	8.84 cm
Displacement Volume	4.3 liter
Compression Ratio	9.3:1

Table II - Engine Driving Cycle

Step	Mode	Time in Mode [Sec]*	Dynamometer Load [kg]	Engine Speed [RPM]
1	Idle	60	0	800
2	City Cruise	150	10	1,500
3	Acceleration	40	25	2,800
4	Heavy HWY Cruise	210	15	2,200
5	Light HWY Cruise	60	10	2,200
6	Idle	60	0	800
7	City Cruise	180	10	1,500
8	Idle	60	0	800

* All steps except step number 3, include a 15 second transition ramp. Step 3 include a 20 second transition ramp.

All of the test runs were made with the same base gasoline, which was representative of commercial unleaded fuel. The results are set forth in Table III.

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Table III				
Laboratory Engine Test Results				
Run	Additive	Concentration, ppm	Intake Valve Deposits, mg	Combustion Chamber Deposits, mg
1	-	-	530	1,455
2	Poly (oxyalkylene) Amine ^a	200	471	1,692
3	Polyalkyl Phenol ^b	400	103	2,530
4	Poly (oxyalkylene) Amine/Polyalkyl Phenol ^c	200/400	18	1,825

a: tetrapropenylphenyl poly(oxybutylene) ethylene diamine carbamate

b: Ultravis 10 polyisobutyl (MW = 950) phenol

c: mixture of 200 ppm tetrapropenylphenyl poly(oxybutylene) ethylene diamine carbamate and 400 ppm Ultravis 10 polyisobutyl phenol

The results shown in Table III demonstrate that the combination of polyisobutyl phenol and tetrapropenylphenyl poly(oxybutylene) ethylene diamine carbamate has a synergistic effect and gives significantly better intake valve deposit control than either component by itself. Also, the addition of tetrapropenylphenyl poly(oxybutylene) ethylene diamine carbamate to the polyisobutyl phenol reduces the combustion chamber deposit weight compared to the polyisobutyl phenol alone.

01 WHAT IS CLAIMED IS:

02

03 1. A fuel additive composition comprising:

04

05 (a) a poly(oxyalkylene) amine having at least one
06 basic nitrogen atom and a sufficient number of
07 oxyalkylene units to render the poly(oxyalkylene)
08 amine soluble in hydrocarbons boiling in the
09 gasoline or diesel range; and

10

11 (b) a polyalkyl hydroxyaromatic compound or salt
12 thereof wherein the polyalkyl group has sufficient
13 molecular weight and carbon chain length to render
14 the polyalkyl hydroxyaromatic compound soluble in
15 hydrocarbons boiling in the gasoline or diesel
16 range.

17

18 2. The fuel additive composition according to Claim 1,
19 wherein the poly(oxyalkylene) amine of component (a)
20 has a molecular weight in the range of about 500 to
21 about 10,000.

22

23 3. The fuel additive composition according to Claim 1,
24 wherein the poly(oxyalkylene) amine of component (a)
25 contains at least about 5 oxyalkylene units.

26

27 4. The fuel additive composition according to Claim 1,
28 wherein the poly(oxyalkylene) amine of component (a) is
29 a hydrocarbyl poly(oxyalkylene) polyamine.

30

31 5. The fuel additive composition according to Claim 1,
32 wherein the poly(oxyalkylene) amine of component (a) is
33 a poly(oxyalkylene) polyamine wherein the
34 poly(oxyalkylene) moiety is connected to the polyamine

- 01 moiety through an oxyalkylene hydroxy linkage derived
02 from an epihalohydrin.
03
- 04 6. The fuel additive composition according to Claim 1,
05 wherein the poly(oxyalkylene) amine of component (a) is
06 a branched alkyl poly(oxyalkylene) monoamine wherein
07 the branched alkyl group is derived from the product of
08 a Guerbet condensation reaction.
09
- 10 7. The fuel additive composition according to Claim 1,
11 wherein the poly(oxyalkylene) amine of component (a) is
12 a hydrocarbyl poly(oxyalkylene) aminocarbamate.
13
- 14 8. The fuel additive composition according to Claim 7,
15 wherein the hydrocarbyl group in component (a) contains
16 from 1 to about 30 carbon atoms.
17
- 18 9. The fuel additive composition according to Claim 8,
19 wherein the hydrocarbyl group in component (a) is an
20 alkylphenyl group.
21
- 22 10. The fuel additive composition according to Claim 9,
23 wherein the alkyl moiety in the alkylphenyl group is
24 tetrapropenyl.
25
- 26 11. The fuel additive composition according to Claim 7,
27 wherein the amine moiety of the aminocarbamate is
28 derived from a polyamine having from 2 to 12 amine
29 nitrogen atoms and from 2 to 40 carbon atoms.
30
- 31 12. The fuel additive composition according to Claim 11,
32 wherein the polyamine is a polyalkylene polyamine
33 having 2 to 12 amino nitrogen atoms and 2 to 24 carbon
34 atoms.

- 01 13. The fuel additive composition according to Claim 12,
02 wherein the polyalkylene polyamine is selected from the
03 group consisting of ethylene diamine, propylene
04 diamine, diethylene triamine and dipropylene triamine.
05
- 06 14. The fuel additive composition according to Claim 7,
07 wherein the poly(oxyalkylene) moiety of component (a)
08 is derived from C₂ to C₈ oxyalkylene units.
09
- 10 15. The fuel additive composition according to Claim 7,
11 wherein the hydrocarbyl poly(oxyalkylene)
12 aminocarbamate of component (a) is an alkylphenyl
13 poly(oxybutylene) aminocarbamate, wherein the amine
14 moiety is derived from ethylene diamine or diethylene
15 triamine.
16
- 17 16. The fuel additive composition according to Claim 1,
18 wherein the polyalkyl hydroxyaromatic compound of
19 component (b) has a polyalkyl group with an average
20 molecular weight of about 400 to 5,000.
21
- 22 17. The fuel additive composition according to Claim 1,
23 wherein the hydroxyaromatic compound is phenol.
24
- 25 18. The fuel additive composition according to Claim 1,
26 wherein the polyalkyl substituent in component (b) is
27 derived from polypropylene, polybutylene, or
28 polyalphaolefin oligomers of 1-decene.
29
- 30 19. The fuel additive composition according to Claim 18,
31 wherein the polyalkyl substituent in component (b) is
32 derived from polyisobutylene.
33
34

- 01 20. The fuel additive composition according to Claim 19,
02 wherein the polyisobutylene contains at least about 20%
03 of a methylvinylidene isomer.
04
- 05 21. The fuel additive composition according to Claim 1,
06 wherein component (a) is an alkylphenyl
07 poly(oxybutylene) aminocarbamate, wherein the amine
08 moiety is derived from ethylene diamine or diethylene
09 triamine, and component (b) is a polyisobutyl phenol.
10
- 11 22. A fuel composition comprising a major amount of
12 hydrocarbons boiling in the gasoline or diesel range
13 and an effective detergent amount of an additive
14 composition comprising:
15
- 16 (a) a poly(oxyalkylene) amine having at least one
17 basic nitrogen atom and a sufficient number of
18 oxyalkylene units to render the poly(oxyalkylene)
19 amine soluble in hydrocarbons boiling in the
20 gasoline or diesel range; and
21
- 22 (b) a polyalkyl hydroxyaromatic compound or salt
23 thereof wherein the polyalkyl group has sufficient
24 molecular weight and carbon chain length to render
25 the polyalkyl hydroxyaromatic compound soluble in
26 hydrocarbons boiling in the gasoline or diesel
27 range.
28
- 29 23. A fuel concentrate comprising an inert stable
30 oleophilic organic solvent boiling in the range of from
31 about 150°F to 400°F and from about 10 to 70 weight
32 percent of an additive composition comprising:
33
34

- 01 (a) a poly(oxyalkylene) amine having at least one
02 basic nitrogen atom and a sufficient number of
03 oxyalkylene units to render the poly(oxyalkylene)
04 amine soluble in hydrocarbons boiling in the
05 gasoline or diesel range; and
06
- 07 (b) a polyalkyl hydroxyaromatic compound or salt
08 thereof wherein the polyalkyl group has sufficient
09 molecular weight and carbon chain length to render
10 the polyalkyl hydroxyaromatic compound soluble in
11 hydrocarbons boiling in the gasoline or diesel
12 range.
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INTERNATIONAL SEARCH REPORT

PCT/US93/02038

A. CLASSIFICATION OF SUBJECT MATTER																				
IPC(5) : C10L 1/22 US CL : 044/387,442,450																				
According to International Patent Classification (IPC) or to both national classification and IPC																				
B. FIELDS SEARCHED																				
Minimum documentation searched (classification system followed by classification symbols) U.S. : 044/387,442,450																				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched																				
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)																				
C. DOCUMENTS CONSIDERED TO BE RELEVANT																				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																		
A	US,A, 3,849,085 (Kreuz et al.) 19 November 1974 See Col. 2, lines 3-61.	1-23																		
A	US,A, 4,134,846 (Machleder et al.) 16 January 1979 See col. 1, lines 36-59 and col. 2 lines 30-64.	1-23																		
A	US,A, 4,191,537 (Lewis et al.) 04 March 1980 See claims.	1-23																		
A	US,A, 4,270,930 (Campbell et al.) 02 June 1981 See the entire document.	1-23																		
A	US,A, 4,778,481 (Courtney) 18 October 1988 See claims.	1-23																		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.																				
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Date of the actual completion of the international search 10 MAY 1993		Date of mailing of the international search report 07 JUL 1993																		
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231		Authorized officer JACQUELINE V. HOWARD																		
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/02038

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 4,881,945 (Buckley, III) 21 November 1989 See the entire document.	1-23
A	US,A, 4,933,485 (Buckley, III) 12 June 1990 See the entire document.	1-23

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